

CHARGE, ORBITAL AND SPIN-STATE ORDERING IN THE PEROVSKITE-BASED COBALTTITES $\text{RBaCo}_2\text{O}_{5+d}$ ($0 \leq d \leq 1$)F. Fauth¹ E. Suard² V. Caignaert³¹European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex FRANCE ²Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex³Laboratoire CRISMAT/ISMRA, 6 Bd Marechal JUIN, F-14050 Caen Cedex

The general class of perovskite-based cobaltites $\text{RBaCo}_2\text{O}_{5+d}$ ($R = \text{lanthanide}$, $0 \leq d \leq 1$) has gained substantial interest since the highest magneto-resistivity (MR) ever observed in Co-based oxides have been reported in $\text{RBaCo}_2\text{O}_{5.4}$ ($R = \text{Eu, Gd}$). Furthermore, this system exhibits a rich phase diagram since it offers the possibility, by varying the oxygen content d , to tune both the oxidation state of cobalt and its oxygen surrounding (pyramidal, octahedral and mixed coordination at $d = 0$, $d = 1$ and $d = 0.5$, respectively). In RBaCo_2O_5 ($R = \text{Y, Tb, Dy, Ho}$), charge ordering of Co^{2+} and Co^{3+} was observed below $T(\text{CO})$ 210 K. In $\text{LaBaCo}_2\text{O}_6$, we have evidenced a Jahn-Teller induced long-range ferrodistorive structure of the CoO_6 network below $T(\text{C})$ 180 K resulting from $d(3z^2-r^2)$ ferro-orbital ordering. Recently, the crystallographic, magnetic and electronic properties of the $\text{NdBaCo}_2\text{O}_{5.47}$ have been investigated using neutron and synchrotron powder diffraction. At $T(\text{MI})$ 360 K, the compound exhibits an associated metal-insulator and HS-Co^{3+} to IS-Co^{3+} spin-state transition. At $T(\text{N})$ 275 K, the IS-Co^{3+} magnetic moments order in a G-type AFM structure, which is typical of these systems. At $T(\text{SSO})$ 235 K, clusters of a different magnetic structure set in within the AFM G-type matrix. This new structure results from the crossover of some IS-Co^{3+} to LS-CoIII and the ordering of the diamagnetic ions over 350 Å correlation lengths. The same electronic phase segregation is observed in different rare-earth compounds $\text{RBaCo}_2\text{O}_{5+d}$ ($R = \text{Dy, Tb, Ho}$) and seems to occur only for a narrow stoichiometry range around $d = 0.5$.

Keywords: ELECTRONIC CONFIGURATION PHASE TRANSITION PEROVSKITE

CRYSTAL STRUCTURE OF SUPERCONDUCTING PYROCHLORE OXIDE $\text{Cd}_2\text{Re}_2\text{O}_7$ T. Kamiyama¹ Z. Hiroi² K. Oikawa¹¹High Energy Accelerator Research Organization ²ISSP, Univ. of Tokyo

Two structural phase transitions were discovered in the first pyrochlore-type superconductor $\text{Cd}_2\text{Re}_2\text{O}_7$. These structural changes are accompanied by dramatic change in resistivity and magnetic susceptibility. To obtain information about the electronic structure and the mechanism of superconductivity, it is crucial to understand the nature of the transitions. Then, the structures of $\text{Cd}_2\text{Re}_2\text{O}_7(\text{Cd-114})$ were studied by a time-of-flight neutron powder diffractometer, Sirius, with supermirror guide ($L = 40$ m) from 9 K to room temperature. Scattering amplitudes of Cd-114 and Re were confirmed by the separate measurements of $\text{CdO}(\text{Cd-114})$ and ReO_3 . The results indicate deformation of ReO_6 octahedra, which can be discussed in relation to electronic structures.

Keywords: CD2RE2O7 NEUTRON DIFFRACTION RIETVELD

NEUTRON DIFFRACTION IN STRUCTURAL CHARACTERIZATION OF COMPLEX OXIDES

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Neutron diffraction is an invaluable technique for characterization of inorganic oxides, particularly when fine structural details are determined by the behavior of oxygen atoms. We have recently developed a novel approach of simultaneous simulated annealing of neutron and X-ray diffraction data and applied it successfully to a number of materials with subtle structural features. BiPb_2VO_6 is a polar, SHG-active material. It displays two polymorphs. α - BiPb_2VO_6 crystallizes in space group Pn , with cell parameters of $a = 7.71529(1)$ Å, $b = 5.84864(1)$ Å, $c = 29.08203(3)$ Å, $\beta = 94.25503(4)^\circ$ and forty atoms in the asymmetric unit. Metal positions were found by direct methods. The structure was completed by simulated annealing of metal coordinates and orientational parameters of VO_4 groups. This approach has allowed us to structurally characterize both polymorphs of BiPb_2VO_6 and to establish a relationship between the two in terms of an order-disorder type phase transition. $\text{Bi}_2\text{Sn}_2\text{O}_7$ is a well-known selective oxidation catalyst. γ - $\text{Bi}_2\text{Sn}_2\text{O}_7$, stable above 690°C , adopts the pyrochlore structure. At room temperature, α - $\text{Bi}_2\text{Sn}_2\text{O}_7$ is pyrochlore-related, but the unit cell is apparently body-centered tetragonal with $a = 15.05$ Å, $c = 21.50$ Å. We have identified twenty possible space groups for α - $\text{Bi}_2\text{Sn}_2\text{O}_7$, starting from the metric $I-4c_2$, by taking into account the unit cell transformations that accompany the γ - β - α phase transitions. We have thus solved the crystal structure of α - $\text{Bi}_2\text{Sn}_2\text{O}_7$ using the method of simulated annealing simultaneously on synchrotron X-ray and neutron diffraction data, followed by conventional Rietveld refinement of the combined data sets. α - $\text{Bi}_2\text{Sn}_2\text{O}_7$ represents one of the more complex crystal structures solved to-date from powder diffraction data.

Keywords: OXIDE MATERIALS, POWDER DIFFRACTION, STRUCTURE SOLUTION

STRUCTURAL STUDIES ON FORMATE DEHYDROGENASE-N FROM *E. COLI*M. Jormakka¹ S. Toernroth² B. Byrne¹ S. Iwata¹¹Imperial College of Science, Technology and Medicine Division of Biomedical Sciences SAF Bulding LONDON SW7 2AZ UK ²Uppsala University

A membrane protein complex, formate dehydrogenase-N (Fdn-N) is a major electron donor to the nitrate respiration system of *E. coli*. This enzyme, together with nitrate reductase (Nar), forms a classical redox loop system through the membrane quinone pool, which translocates protons across the membrane. A three-dimensional structure of Fdn-N has been determined using MAD technique to 1.6 Å resolution, the highest resolution of a membrane protein complex to date. This high resolution study revealed the trimeric structure of this 170 kDa enzyme, which consists of two molybdopterin guanine dinucleotide cofactors, selenocysteine, molybdenum, five 4[4Fe-4S] clusters, two haem bs, HQNO (a menaquinone analogue) and cardiolipin. The structure clearly demonstrates how electron transfer and proton translocation are coupled in this enzyme and in the Fdn/Nar system. The structure was also successfully employed to explain some important biochemical and biophysical features of related enzymes, nitrate reductase and [NiFe]-hydrogenase.

Keywords: FORMATE DEHYDROGENASE MEMBRANE PROTEIN HIGH RESOLUTION